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(54) Title: SEALER COATING FOR USE ON POROUS LAYERS

(57) Abstract: A die or mould coating comprising: a bond layer and a porous layer of ceramic material produced by co-deposition and heating of said ceramic material and a powder of an organic thermosetting polymer material; and an upper sealer coating comprising metal or ceramic filler particles dispersed in a carrier.

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## SEALER COATING FOR USE ON POROUS LAYERS

### Technical Field

This invention relates to sealer coating compositions that are suitable for use on die coatings and in particular ceramic die coatings.

### 5 Background of the Invention

The role of coatings used on substrates in contact with molten metal is to are control heat flow through the coating and prevent premature solidification of the molten metal in the die cavity. Additionally, thicker insulating coatings tend to increase the thermal mismatch between the coating and substrate increasing the stress on the coating and resulting in spalling of the coating.

Improved die coatings are disclosed in PCT/AU00/00239, the whole contents of which are incorporated by reference. These compositions have particular application on low pressure and gravity die casting. Prior to the above invention the surface of each metal mould or die component, which is to be contacted by molten metal, was usually coated by a commercial die coat. A ceramic-based coating was typically used at a thickness of from about 0.05 to 1.0mm. By referring to the coatings as "ceramic-based" the term "ceramic" was used in its art recognised sense as being inorganic, non-metallic materials processed or consolidated at higher temperature" (McGraw-Hill Encyclopaedia of Science and Technology 1994). The classes of materials generally considered to be ceramics are oxides, nitrides, borides, silicides and sulfides. Intermetallic compounds such as aluminates and beryllides are also considered as "ceramics" as are phosphides, antimonides and arsenides. The main function of the ceramic-based coating was to provide a degree of insulation which was intended to prevent premature solidification of the molten metal, and thereby enable the complete filling of the die cavity before solidification started. However, the coating also was to protect the die surfaces from erosion or corrosion by impingement or contact with the molten metal.

Previously known die coating technology involved the use of a water-based suspension of ceramic particles containing a water-based binder, most commonly sodium or potassium silicate. Coating mixtures of this type needed to be properly stored and mixed. The coating was applied to the prepared surface of a die

component using a pressurised air spray gun. For this, the die component was preheated, typically from about 150° to 220°C, such that water was evaporated from the die surface, enabling the binder to polymerise or cure and bond the ceramic particles together and to the die surface.

5       The die coatings produced with these known aqueous ceramic suspensions were highly porous. The level of porosity typically ranged from about 30 to 60%, depending on the size and shape of the ceramic particles and the proportion of binder used. High porosity gave the coating very good insulating properties. However, the strength of the coatings was limited by the strength of the binder  
10       used (about 6.9 MPa in the case of sodium silicate) and the level of porosity of the coating.

      The invention of PCT/AU00/00239 provided an improved die coating for use on the surface of a mould or die component contacted by molten metal in low pressure or gravity die casting. The coating included a porous layer of ceramic  
15       material produced by co-deposition, using a thermal spraying procedure, of a powder of the ceramic material and a powder of a suitable organic polymer material and, after the co-deposition, heating of the polymer material to cause its removal. In that specification the term "ceramic material" was used very broadly but consistent with the definition in this technology field, outlined earlier.

20       While the above invention provided good performance on a range of mould and die situations, problems arise particularly, but not exclusively in low draft angle areas of a die or mould. Drafts (or taper) in a mould facilitate part removal from the mould. The draft is in the offset angle in a direction parallel to the mould opening. It is generally best to allow for as much draft as possible for easy release  
25       from the mould. A common recommendation is to allow 1 to 3 degrees of the draft.

      In low draft areas of a mould that is where the draft angle is less than 2°, particular problems can arise from the use of insulating coatings as described above.

      Following solidification of molten metal in the die, molten metal solidifies  
30       into the pores of the ceramic layer. This results in not only an unsatisfactory finish on the die casting, but causes a great deal of drag and stress on the surface of the

porous layer when the casting is removed. This surface drag considerably reduces the potential service life of the coating.

### Summary of the Invention

The applicants have found that by applying a sealer coat having filler  
5 particles which fill and seal substantially all of the surface pores, the problem of metal solidifying in the pores is avoided and the service life of the layer is greatly improved.

Accordingly, the invention provides in one form an improved die or mould  
coating comprising a porous layer of ceramic material produced by co-deposition  
10 of a powder of the ceramic material and a powder of a suitable organic polymer material and, an upper sealer coating comprising metal or ceramic filler particles dispersed in a carrier.

The application of a sealer coat is particularly beneficial in low draft areas of  
mould cavities, although it is also useful in sealing mould or die components which  
15 do not have a low draft angle.

The porous ceramic layer produced by the co-deposition is heated to a  
temperature up to 550°C to thermally decompose and remove the polymer  
material prior to application of the upper sealer coating.

The porous ceramic layer preferably has a porosity of 5 to 70% after the  
20 polymeric material is removed.

The carrier for the metal or ceramic filler particle may be a low friction co-  
efficient carrier and is preferably a heat resistant resin such as silicone.

The filler particle, preferably, on average have a particle 50% smaller than  
the pore size found on the surface of the ceramic porous layer and of suitable  
25 composition to provide wear resistance and lubricating properties to the sealer.

The size of the filler particles will depend on the size of the polymer  
molecules which are removed by the thermal decomposition process but are  
typically in the range of 5 to 200µm. Suitable metal and ceramic filler particles are  
selected from the group of tungsten, borides, nitrides silicides and carbides. The  
30 sealer coating may contain volatile components such as organic solvents including

toluene or xylene to allow the viscosity of the sealer coating to be modified to that suitable for application.

Further features, objects and advantages will become more apparent from the following detailed description of the invention and Examples.

## 5        **Detailed Description of the Invention**

To enhance the adhesion of the porous ceramic layer to the substrate, a bond coat is preferably applied to the metal substrate. In one form, the bond coat is of substantially uniform thickness over all surfaces of the metal substrate, the mould or die components which define the die cavity.

10        The applicants have further found that in many cases, the application of a bond coat to the metal die prior to application of the porous layer, provides better adhesion of the porous layer to the metal die and reduces the thermal mismatch between the die and the ceramic coating, further increasing the service life of the coating and protecting the surface of the mould or die. The bond coat also serves  
15        to enhance the adhesive strength of the coating.

The bond coat preferably is formed of a metallic, intermetallic or composite particulate materials. The bond layer is formed from a particulate material applied to the surface of the metal surface of the mould. The bond coat layer can be applied by a thermal spray process such as vacuum plasma spray (VPS) ,  
20        atmospheric plasma spray (APS), combustion flame spraying and hyper velocity oxyfuel (HVOF) spray processes.

The metal in the bond coat may be in the metallic, intermetallic, oxide, clad or alloyed form consisting of any one or more of the metal components selected from the group of Mo, Ni, Al, Cr, Co, Y and W and may be in combination with  
25        yttria, alumina, zirconia, boron, carbon and have a particle size in the range of 5 to 250 $\mu$ m, typically 40 to 125 $\mu$ m. The bond coat preferably has a thickness of 5 to 300 $\mu$ m with a substantially uniform coating layer being provided over the surfaces to have the porous ceramic coat applied.

An example of a bond coat powder was a Metco 480-NS grade fully alloyed  
30        spheroidal, gas atomised Nickel 95% Aluminium 5% for which the data sheet indicated a particle size range of not more than 90 $\mu$ m and not less than 45 $\mu$ m.

The polymer and ceramic particles are then co-deposited onto the bond coat and the co-deposited layer is heated to a temperature up to 550°C to thermally decompose and remove the polymer material prior to application of the upper sealer coating.

5        The ceramic powders which are used in providing the porous coating may be a processed powder conventionally used in the production of ceramic articles. Thus, the powder may be selected from at least one metal compound such as oxides, nitrides, carbides and borides. Suitable examples include carbon, alumina, titania, silica, stabilized zirconia, silicon nitride, boron nitride, silicon carbide,  
10 tungsten carbide, titanium borides and zirconium boride. However, the ceramic powder may be of a suitable mineral origin such as clay minerals, hard rock ore and heavy mineral sands such as those of ilmenite, rutile and/or zircon. One particularly suitable powder is that obtained from scoria or pumice, since powder particles of these materials are internally porous and have the added benefit of  
15 being of angular form.

A wide range of plastics and like materials can be used to provide the organic polymer powder. Important requirements for selection of these are availability in a suitable powder form and an ability to withstand sufficiently the temperatures to which they are exposed during thermal deposition. A further  
20 requirement is an ability to be combusted or decomposed at practical temperatures and in practical reaction times. In large part, the materials comprise thermoplastics, such as polystyrene, styrene-acrylonitrile, polymethacrylates polyesters, polyamides, polyamide-imides and PTFE.

The respective powders, that is the ceramic powder and the polymer  
25 powder, preferably are of a relatively narrow size spectrum. In general, they preferably are of particle sizes not more than about 60  $\mu\text{m}$  and not less than about 1  $\mu\text{m}$  in the case of the ceramic and not less than about 5  $\mu\text{m}$  in the case of the polymer material.

In practice the upper sealer coating is applied to the porous layer after the  
30 polymer has been removed from that layer. The porous layer typically then has a porosity of 5 to 70%, and the surface of this layer is characterised by a plurality of pores. The sealer coating may be applied with a paint brush, air spray gun or other

application means. To achieve suitable viscosity for application a number of volatile diluents may be used. It will be appreciated that relatively volatile diluents are preferred so that the sealer coating effectively penetrates the porous layer and virtually produces a smooth surface which seals the surface from the penetrating molten metal. It is preferred that the carrier is heat resistant so that it is not substantially damaged by the molten metal and so that it can also be applied when the die is hot. The carriers may include crosslinking agents, such as silicone or may be themselves crosslinkable.

Preferably the film thickness of the upper sealer coating is in the range 5 to 100  $\mu\text{m}$  and more preferably approximately 10  $\mu\text{m}$ .

The invention will be further described by reference to the following non limiting example.

#### **Example 1**

This Example describes the formation of a mould coating composition on a metal surface of a die having low draft regions.

Miller Thermal SG 100 Plasma Spray Torch thermal spray unit. The bond coat powder was a Metco 480-NS grade fully alloyed spheroidal, gas atomised Nickel 95% Aluminium 5% for which the data sheet indicated a particle size range of not more than 90 $\mu\text{m}$  and not less than 45 $\mu\text{m}$ . The process settings used were as follows: -

Voltage:	33
Current:	650
Plasma Gases:	Argon at 50 psi & Helium at 50 psi
Powder Feed Rate:	11.5 RPM at 35 psi
Spray Distance:	100mm

Then the ceramic powder and polymer powder were mixed and subjected to a thermal spraying to form a co-deposited coating on a ladle used for transferring molten metal to a die cavity defining the surface of a low pressure metal die cast component. The ceramic powder was Metco 210 (NS/NS-1/NS-1-G) grade zirconia stabilised by 24% magnesium oxide for which the data sheet

indicated a particle size range of not more than  $90\mu\text{m}$  and not less than  $11\mu\text{m}$ , a melting point of  $2140^{\circ}\text{C}$  and a density of  $4.2\text{gcm}^{-3}$ . The polymer powder was of polymer supplied by Sulzermetco which had been ground to  $-150 + 45\mu\text{m}$  ( $-100 + 325$ ). The powder mixture of  $\text{MgO}(24\%)$   $\text{ZrO}_2/\text{polystyrene}$  contained 15 %  
5 volume percent (3wt%) of polymer.

The co-deposition of the powder mixture was performed using a Miller Thermal SG 100 Plasma Spray Torch and a Miller Thermal powder feeder, under the following settings:

	Voltage:	34
10	Current:	750
	Plasma Gases:	Argon at 50 psi & Helium at 50 psi
	Powder Feed Rate:	2.88 (rpm) at 35 psi
	Spray Distance:	100 mm

Following co-deposition of the blended powders, the deposited coating was  
15 heated to  $450^{\circ}\text{C}$  for one hour to cause the polymer to decompose. As well as plasma application other thermal application techniques may also be used. A commercial sealer coating composition, Metcoseal SA (Sulzer Metco consisting of aluminium flakes and silicone binder, was applied by paintbrush to the low draft regions to form a coating approximately  $25\mu\text{m}$  thick. After evaporation of the  
20 sealant a sealer coat was formed. A number of castings were produced from molten aluminium in the mould and it was observed that in the low draft region of the mould, the mould coating composition was largely undamaged. This allowed the mould to be used for many more moulding operations than if the sealer coating was not used.



**CLAIMS**

1. A die or mould coating comprising:  
a bond layer and a porous layer of ceramic material produced by co-deposition and heating of said ceramic material and a powder of an organic  
5 thermosetting polymer material; and  
an upper sealer coating comprising metal or ceramic filler particles dispersed in a carrier.
2. The die or mould coating of claim 1, wherein the porous layer has a porosity  
10 of 5 to 70%.
3. The die or mould coating of claim 1, wherein the porous layer has a thickness in the range of 50µm to 1µm.
- 15 4. The die or mould coating of claim 1, wherein ceramic material in the porous layer is at least one compound selected from the group of carbon, alumina, titania, silica, stabilized zirconia, silicon nitride, boron nitride, silicon carbide, tungsten carbide, titanium borides and zirconium boride.
- 20 5. The die or mould coating of claim 1, wherein the organic polymer material is at least one compound selected from the group of polyester, polystyrene, styrene-acrylonitrile, polymethacrylates polyesters, polyamides, polyamide-imides and PTFE.
- 25 6. The die or mould coating of claim 1, wherein the metal or ceramic filler particles of the upper sealer coating is ceramic particles selected from the groups consisting of borides, nitrides, silicides and carbides or any metal particles including tungsten and aluminium.

7. The die or mould coating of claim 1, wherein the carrier for the metal or ceramic filler particles of the upper sealer coating is a heat resistant resin selected from the group of silicone resins.
- 5 8. The coating of claim 1, wherein the bond layer is applied in a substantially uniform thickness over the metal surfaces of the mould or die components which define a die cavity.
9. The coating of claim 1, wherein the thickness of the sealer coating is in the  
10 range of 5 to 100 $\mu$ m.
10. The coating of claim 1, wherein the thickness of the sealer coating is in the range of 5 to 10 $\mu$ m.
- 15 11. The coating of claim 6, wherein metal or ceramic filler particles, on average have a particle which is 50% of the average size of the pores.
12. The coating of claim 6, wherein the size of the metal or ceramic filler particles is in the range of 5 to 200 $\mu$ m.
- 20 13. A method of forming a coating on a die or mould component comprising the steps of:
- applying a bond layer to the die or mould component;
  - co-depositing a layer of a powder of ceramic material and a powder of an  
25 organic polymer material on to the coated die or mould component;
  - heating the co-deposited layer to bind the ceramic material and thermally decompose the organic polymer material to form a porous ceramic layer; and
  - applying an upper sealer coating comprising metal or ceramic filler particles dispersed in a carrier.

14. The method of claim 13, wherein the co-deposited layer is heated to a temperature up to 550°C to thermally decompose and remove the polymer material.

5 15. The method of claim 1, wherein the bond layer is applied in a substantially uniform thickness over the metal surfaces of the mould or die components which define a die cavity.

16. The method of claim 1, wherein the thickness of the sealer coating is in the  
10 range of 5 to 100µm.

17. The method of claim 1, wherein the thickness of the sealer coating is in the range of 5 to 10µm.

15 18. The method of claim 6, wherein metal or ceramic filler particles, on average have a particle which is 50% of the average size of the pores.


19. The method of claim 6, wherein the size of the metal or ceramic filler particles is in the range of 5 to 200µm.

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20. The method of claim 13, wherein the coating is applied to low draft areas of a die or mould.

# INTERNATIONAL SEARCH REPORT

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
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According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC7 as above		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent WPI: IPC7 as above and ceramic or oxid+ or nitrid+ or borid+ or silicid+ or sulfid+ or aluminat+ or beryllid+		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Patent Abstracts of Japan JP 62-064449 A (Topy Ind Ltd) 23 March 1987 Abstract	
A	Patent Abstracts of Japan JP 07-256389 A (Mazda Motor Corp) 9 October 1995 Abstract	
A	Patent Abstracts of Japan JP 62-054543 A (Yoshikawa Kogyo Co Ltd) 10 March 1987 Abstract	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 25 July 2003		Date of mailing of the international search report - 4 AUG 2003
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**INTERNATIONAL SEARCH REPORT**

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<b>C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2001/0052406 A1 (Kubota et al) 20 December 2001 Whole Document	
A	US 5944088 A (Feagin) 31 August 1999 Whole Document	
A	US 4703806 A (Lassow et al) 2 November 1987 Whole Document	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

**PCT/AU03/00835**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member			
JP	62064449	NONE				
JP	7256389	NONE				
JP	62054543	NONE				
US	2001005240	JP	2001185404			
US	4703806	CA	1310805	EP	252862	JP 63115644
		JP	8276241			
US	5944088	US	5535811	US	5630465	US 5712435
		US	5738819	CA	1339184	
						END OF ANNEX